

McCrone Analysis of COT Wire

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A visit was made to McCrone Associates, Inc on Tuesday March 30, 2004 to analyze deposits of COT wires. Our primary host was Wayne Niemeyer. Kent Rhodes did the XPS analysis and Gretchen did the FTIR analysis

The following samples approximately one inch long were analyzed: a length of new wire, a length of aged wire from SL2_S0 (z=100-105cm), a length of aged wire from SL4_S6 (z=100-110cm), and a length of SL4_P8 (z=100-110cm). Also examined were strands of copper wool that included a bright copper colored piece and a dark purple discolored piece.

EDS RESULTS FROM WIRE SAMPLES (Using JXA-8900RL)

The first test done was Energy Dispersive Spectroscopy (EDS) which scans the sample with an electron beam micro-probe. The electron beam ejects electrons from inner shells of the atoms in the sample and the energy of the x-rays generated when these vacant states are refilled give an indication of the elemental makeup of the sample. The percentages quoted are atomic percentages. (Note: WDS is similar except that it measures the wavelength of the photon with a diffraction grating type technique giving a higher resolution for a more limited energy range.)

The sample of new wire showed primarily the gold coating: the atomic percentages were 32.1% carbon (2.9% by weight) and 65.4% gold (96.8% by weight) at 10keV. The energy spectrum of x-rays is shown in figure 1. There was carbon on all the samples which at this low level was thought to be mostly background. A few dust particles were seen that contained elements other than carbon and gold such as sodium, silicon, or calcium. At 30keV the electron beam could penetrate the gold plating and tungsten could be seen.

The sample of SL2_S0 wire showed a fairly uniform coating that consisted of 89.6% carbon, 4.2% oxygen, and 6.1% gold at 5keV accelerating voltage for the electron beam. The energy spectrum of the generated x-rays is shown in figure 2. When the voltage was increased to 10keV, the electron beam was better at penetrating the coating and more gold was seen: 83.1% carbon, 4.5% oxygen, and 11.8% gold. The associated energy spectrum is shown in figure 3. There were many 2-3 micron wide nodules apparent on the coating and when they were analyzed, the measured percentage of carbon increased. The x-ray spectrum for nodule 1 at 10keV is shown in figure 4. It had 93.1% carbon, 4.1% oxygen, and 2.8% gold. The spectrum for nodule 2 is shown in figure 5. It measured 92.9% carbon, 3.3% oxygen, and 3.7% gold at 10keV. Junk that was probably dust was occasionally seen.

The sample of SL4_P8 looked similar to new wire. The spectrum for a typical area is shown in figure 6. The elemental makeup was 34.3% carbon, 2.3% oxygen, and 63.0% gold at 10keV. This wire had some nodules with 70-75% carbon, but many were clearly dust or dirt with silicon, oxygen, carbon, sodium, calcium, etc.

The SL4_S6 wire showed a fairly uniform coating similar to SL2_S0, but with fewer nodules. The spectrum for an overview area probed at 10keV is shown in figure 7; the measured atomic makeup was 81.4% carbon, 1.5% oxygen, and 17.1% gold suggesting that the coating was thinner than for the SL2_S0 sample. We found a large bright spot (compared to nodule sizes) that was consistent with no coating (probably knocked off in handling). This bright spot had 35.8% carbon, 1.8% oxygen, .9% silicon, and 60.9% gold at 10keV which is close to the results for the new wire. The spectrum for the bright spot is shown in figure 8. There was a nodule that was measured as having 73.8% carbon, 1.9% oxygen, and 24.3% gold at 10keV which is less carbon than measured in the overview area. The spectrum is shown in figure 9. Again there were spots that looked more like dust. The spectrum for one is shown in figure 10 where Cr, Fe, Ni, and Si are seen.

Silicon content wasn't generally listed above for two reasons. There is extremely little of it in all the COT wire samples, and at that level it can be confused with some slight sensitivity to W. For completeness, atomic % of silicon is listed here for the above samples along with their sigma in % of the reading: New Wire 10kV, 0.14% (sigma=52%); SL2_S0 5kV, 0.12% (62%); SL2_S0 10kV, 0.57% (20%); SL2_S0 nodule 1 10kV, 0.04% (54%); SL2_S0 nodule 2 10kV, 0.08% (29%); SL4_P8 10kV, 0.36% (53%); SL4_S6 10kV, 0.05% (115%); SL4_S6 bright spot 10kV, 0.89% (20%); SL4_S6 nodule, 0.04% (218%).

The copper wool strands were also examined with EDS. Strands with little or no discoloration showed 15-18% carbon, 5-8% oxygen, and 74-80% copper at 10keV. A typical spectrum is shown in figure 11. The spectrum from a dark strand is shown in figure 12 and it shows 57.0% carbon, 8.0% oxygen, and 34.8% copper at 10keV. It was surprising that the main contaminant was carbon instead of oxygen.

Using the EDS electron probe, a picture of the wire surface can be determined by looking at the secondary x-rays or backscattered electrons and correlating their intensity with the electron beam position during the scan. Looking at the backscattered electrons gives a picture where low Z material comes out dark and high Z material is bright. Dark nodules were particularly prevalent on SL2_S0 using this technique. Pictures made for the four wire samples are shown in figure 13.

XPS SCANNING TO GET MOLECULAR BONDS

The XPS measurement irradiated the samples with 1400eV x-rays and an energy scan was made of the secondary electrons emitted. A complete scan is done to get a survey of all the elements in the sample and then a precision scan is made of a small energy region to get information on the molecular bonds. This technique only probes the first few nmeters of the sample. One piece of new wire and a piece of SL2_S0 (z=100-105cm) were examined by this method.

The new wire had high gold content with a trace of carbon and oxygen. The spectrum indicated 62.0% C1s, 21.0% O1s, 15.9% Au4f, and 1.1% NaKLL. Kent Rhodes indicated that the

carbon and oxygen traces at this level could be absorbed from airborne species or may possibly be some residual from the wire drawing process.

The SL2_S0 wire had large oxygen and carbon peaks with no gold. The measured amounts were 80.8% C1s, 18.8% O1s, 0.4% NaKLL. Since the XPS scan only probes the first 5-10 nmeters, gold was not expected to be seen. Figure 14 shows the broad scan for both the new wire and the SL2_S0 sample.

A high resolution scan was done in the region of the C1s peak on the SL2_S0 wire. The results of the precision scan were given in units of %Area. The scan found 82% CC,CH; 14% C-O; and 3% C=O. The C-O percentage was significant and the oxygen presumably comes from the alcohol. The results from this precision scan are shown in figure 15.

The XPS apparatus can also be used to etch away the surface area with singly charged argon ions. The energy can be varied from a few hundred eV to a few keV. A thickness of about 5 nmeters was etched away from our sample using 500eV argon ions. This is primarily an attempt to make sure that we are not measuring surface contamination. The precision C1s spectrum after etching is shown in figure 16. The results were 88% CC, CH; 10% C-O, and <1% for C=O.

Kent noted that if one used Auger electrons to probe the surface instead of X-rays, one could get a similar analysis of a small point on the surface, such as one of the nodules. The XPS focus is about 20 microns, half the diameter of the wire.

FESEM HIGH RESOLUTION PICTURES OF THE SURFACES (JSM-6301FXV)

Field Effect Secondary Emission Scanning (FESEM) uses an electron beam making it similar to the EDS analysis. However in this instrument, the electron beam starts from a point field emission source producing a very narrow, well defined electron beam. Secondary electrons are monitored to give a high spatial resolution picture of the surface features.

Several pictures were made. Figure 17 shows a sample of new wire. Figure 18 shows the coating on a typical region of the SL2_S0 sample with lots of sub-micron nodules. Figure 19 shows a relatively rare larger nodule. Figure 20 shows a scraped area of the SL2_S0 wire. In the foreground the bare wire can be seen; behind this area is a smooth dark coating about 300 nmeters thick with lots of sub-micron nodules. The background at the top of the picture is the black tape that was used to secure the sample.

The SL4_S6 wire appeared to also have a film coating. It is shown in figure 21. The striations in the wire were more apparent through the film indicating that it was not as thick as for SL2_S0. Also there were fewer nodules on the coating.

The SL6_P8 wire had a region where the gold coating appeared to be scraped off. Also, there was a spot where there appeared to be lots of dark "dirt" type particles that is shown figure 22. (Wayne had trouble mounting this wire and it may have taken quite a beating.) In general, the surface looked similar to the new wire.

The Cu strands had so many striations that it was difficult to analyze the FESEM picture.

FTIR ANALYSIS

Fourier Transform Infrared analysis was done on the SL2_S0 wire to learn more about the molecular makeup of the coating. This type of reflection spectroscopy irradiates the sample with a broadband infrared beam. The surface is penetrated a short distance by the infrared rays and the reflected spectrum is examined for dips associated with absorption by the sample. Wavenumbers from 4000 to 1000 cm^{-1} were analyzed.

A dark copper wool strand was measured first but nothing was learned, probably due to the rough nature of the surface.

The reflected spectrum for the SL2_S0 wire is shown in figure 23. It has the following features: a broad dip near 3365 cm^{-1} associated with the OH bond (stretching); sharper dips at 2958, 2931, and 2870 cm^{-1} associated with CH₂ and CH₃ bonds; two small dips near 2300 cm^{-1} probably associated with background CO₂; and two small dips at 1734 and 1698 cm^{-1} associated with the C=O bond. There was considerable ringing in the system for wavenumbers beyond 2000 cm^{-1} , so it was difficult to tell what was happening in this region.

Simple aliphatic hydrocarbon strings (either straight or branched) have no oxygen, so what we have appears to be more complicated. (The OH bond is found in water or alcohol samples).

Although the CH and OH bonds are found in our drift gas mixture, they could conceivably be from a contaminant, such as an aliphatic oil.

RAMAN ANALYSIS

An attempt was made to do Raman analysis on our SL2_S0 sample. In Raman analysis, the sample is irradiated with a laser beam and the inelastically scattered light spectrum is analyzed for evidence of the excitation of molecular states. In our case too much background fluorescence prohibited identification of surface compounds.

4/6/04

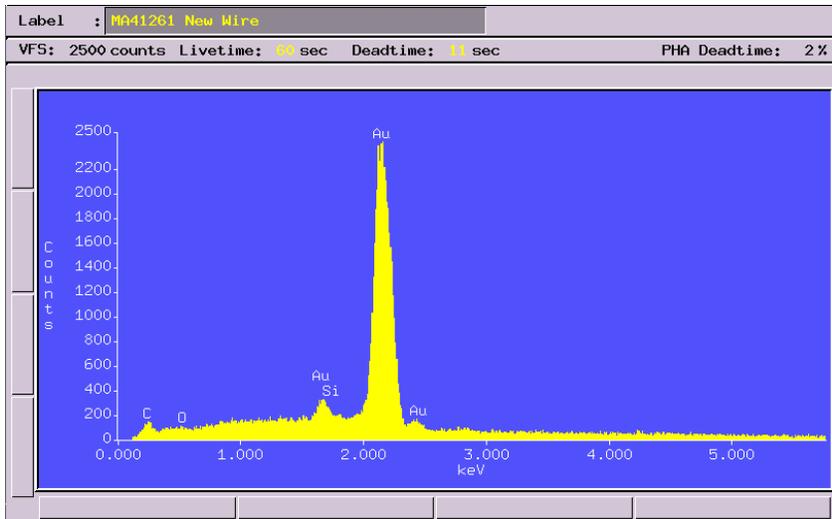


Figure 1 EDS spectrum for a new wire at 10keV. Mostly Au with a little C. Insignificant O and Si.

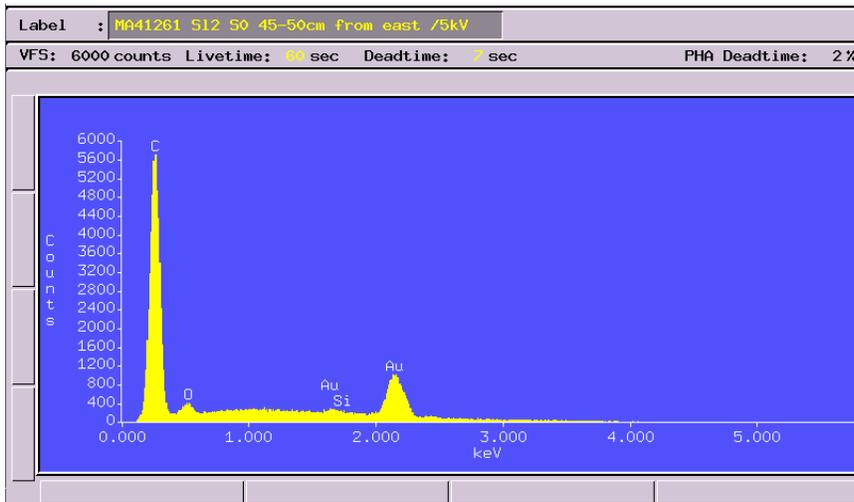


Figure 2. EDS x-ray spectrum of SL2_S0 wire at 5keV. Mostly C with some O and some Au.

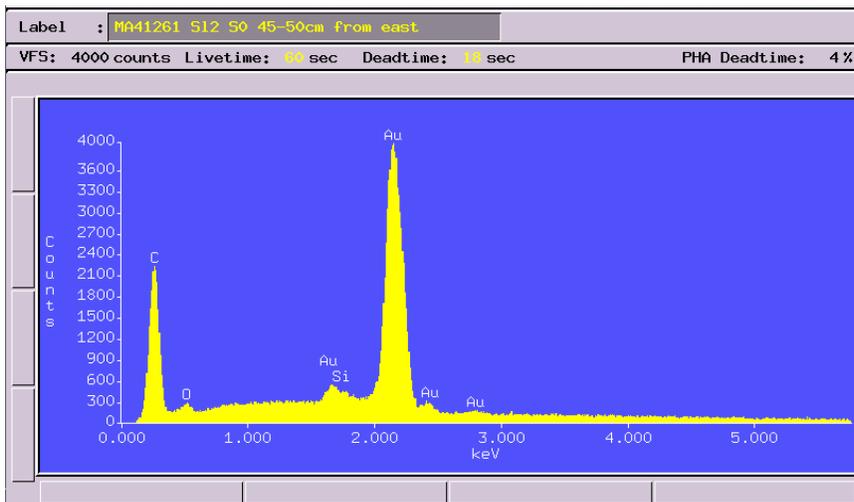


Figure 3 EDS spectrum for SL2_S0 wire at 10keV. Higher energy electrons see more Au.

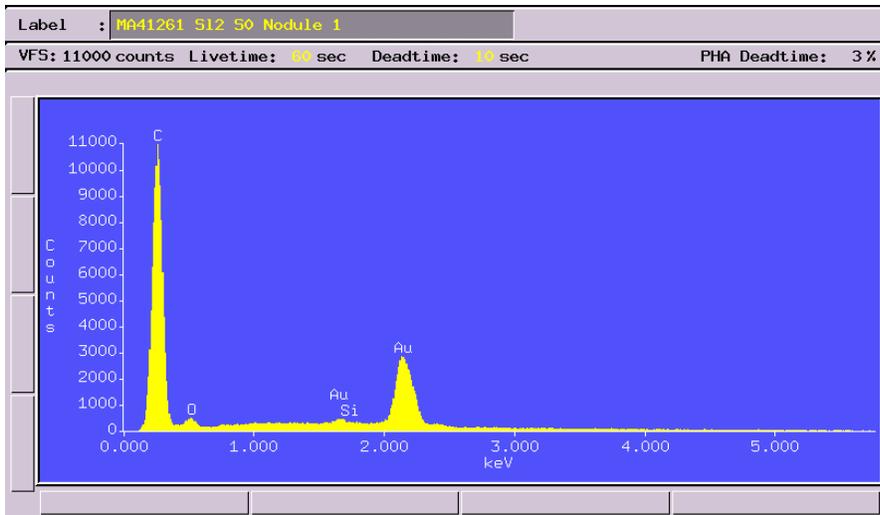


Figure 4 EDS spectrum for nodule 1 on SL2_S0 wire at 10keV. More C and O seen,

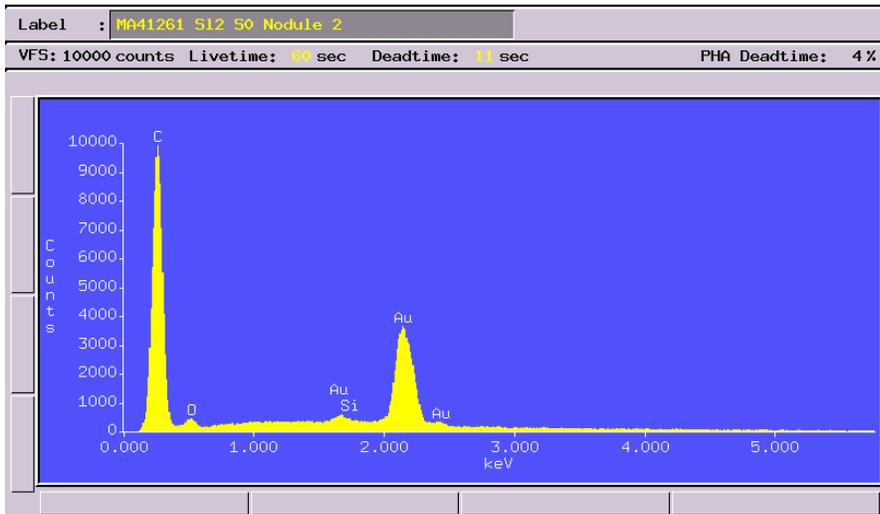


Figure 5 EDS spectrum for nodule 2 on SL2_S0 wire at 10keV. Similar to figure 4.

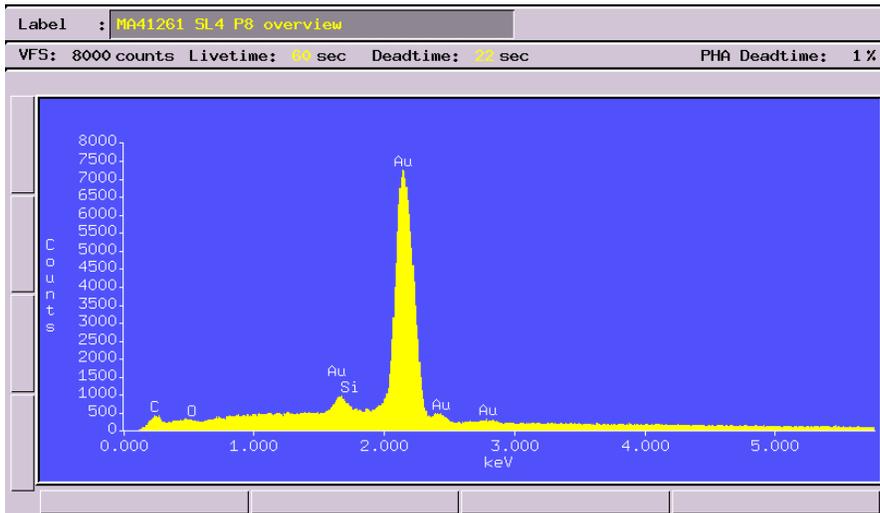


Figure 6 EDS spectrum for SL4_P8 wire at 10keV. Similar to new wire with mostly Au and a little C.

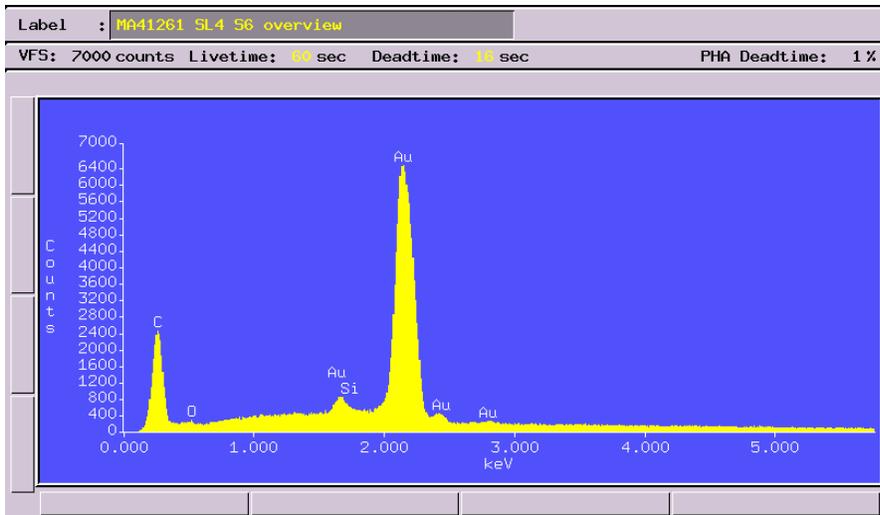


Figure 7 EDS spectrum for SL4_S6 wire at 10keV. Similar to SL2_S0 wire but with thinner coating.

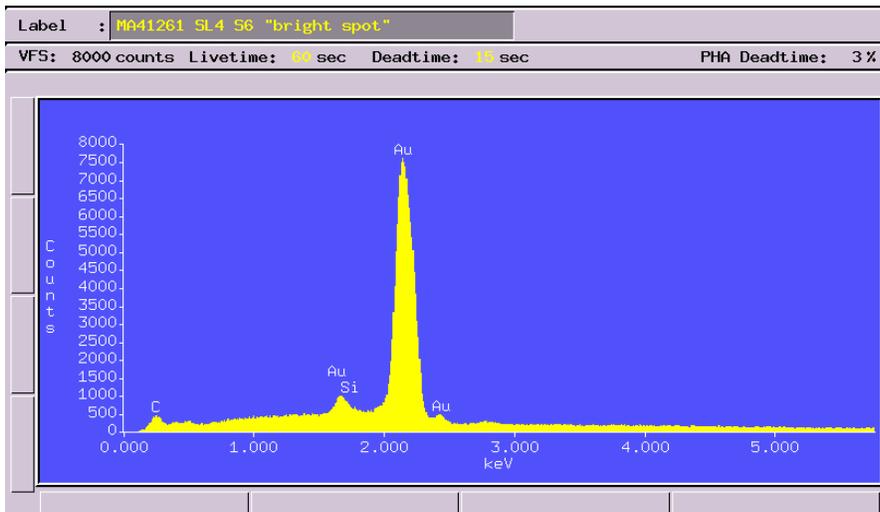


Figure 8 EDS spectrum for SL4_S6 wire at 10keV. Taken at bright spot, looks similar to a new wire.

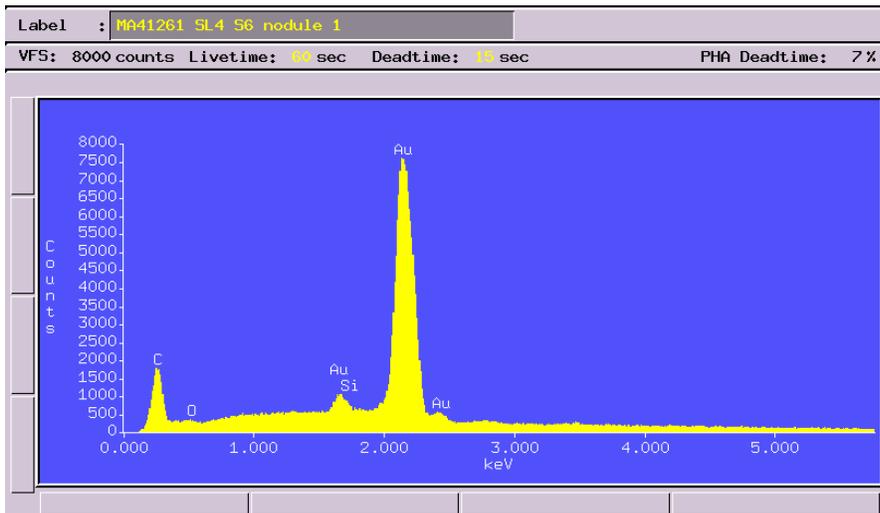


Figure 9 EDS spectrum for SL4_S6 nodule at 10keV. Similar to the general coating.

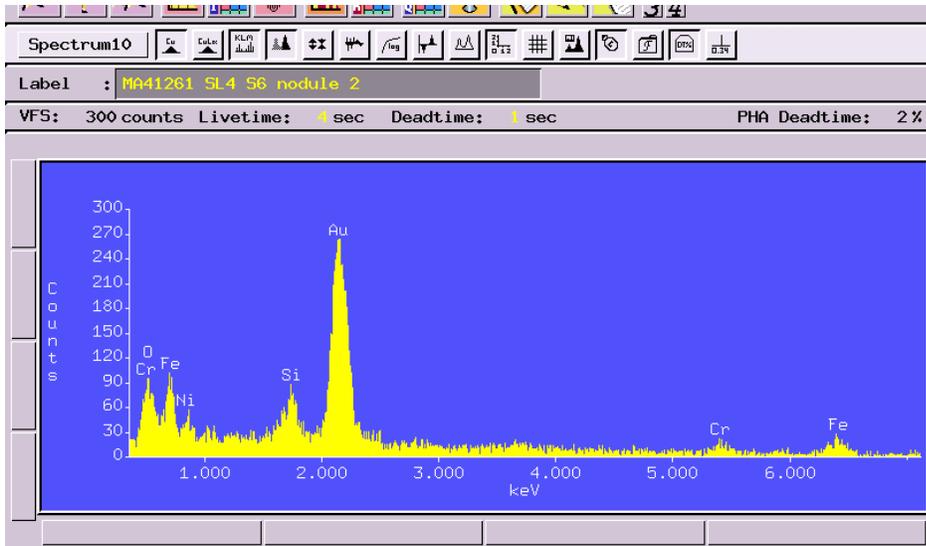


Figure 10 EDS spectrum for SL4_S6 nodule at 10keV. This is probably a dirt speck.

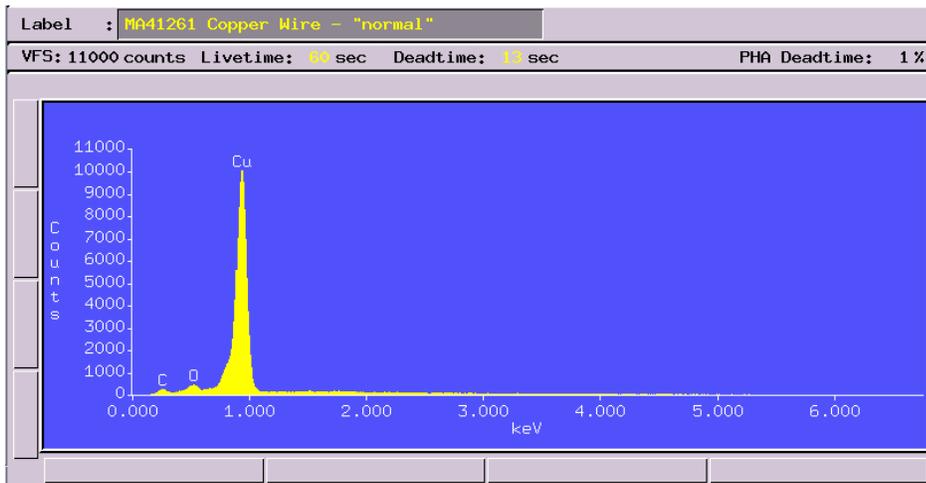


Figure 11. EDS spectrum for a bright copper strand taken from copper wool filter.

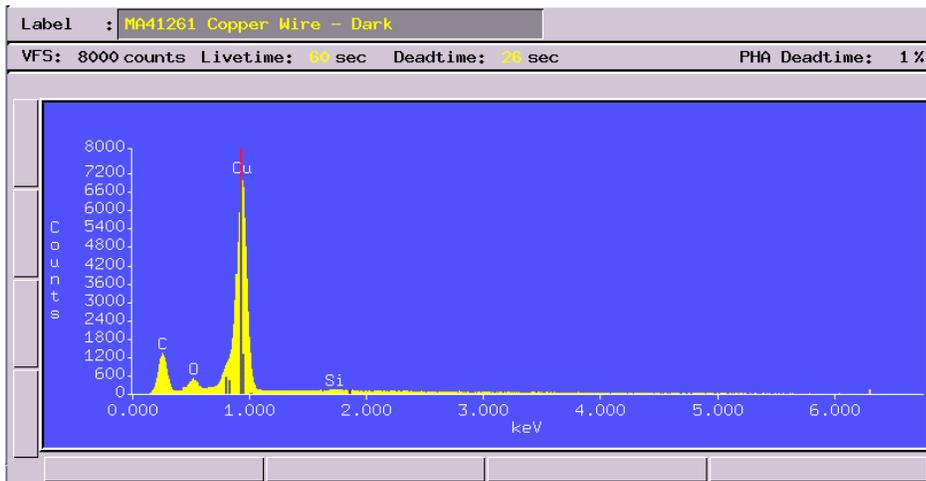


Figure 12. EDS spectrum from dark copper stand. It has significant amounts of C.

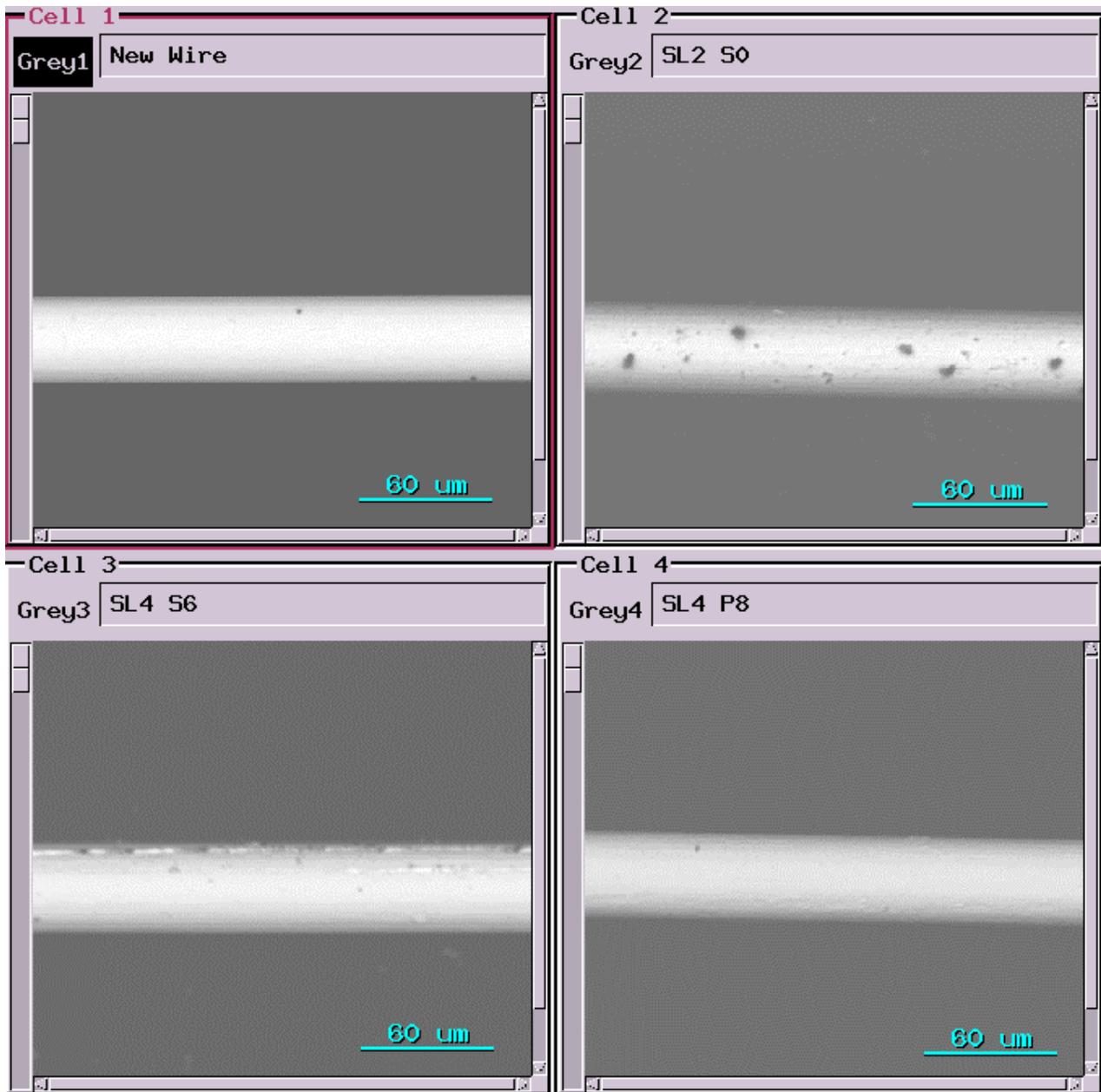


Figure 13. Pictures from the different wire samples using backscattered electrons from the EDS probe. In these pictures, areas of low Z appear darker and areas of high Z appear brighter.

surveys102.spe: Samples 03-30-2004.: as received
 2004 Mar 30 Al mono 2.4 W 10.0 μ 45.0° 187.85 eV 2.030e+03 max 8.75 min
 Su1/Point2: SL2 50, Point 1/1 (SG5 SG5 SG5)

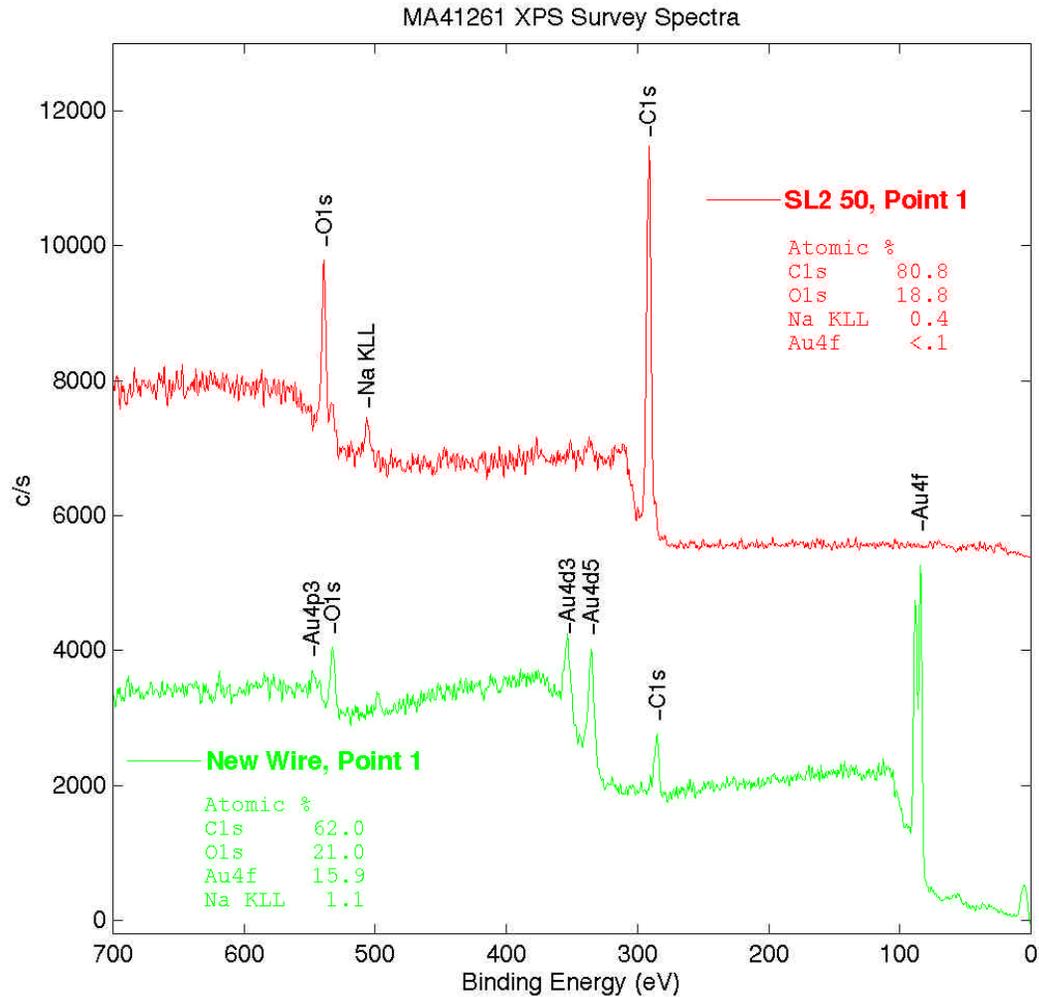


Figure 14. The broad energy spectra from a new wire sample and SL2_S0 sample using XPS analysis. The green is for the new wire and the red is for the SL2_S0 sample. The x-ray from the XPS probe only penetrates a few nanometers.

hrscans103.spe: Samples 03-30-2004.: as received
 2004 Mar 30 Al mono 2.4 W 10.0 μ 45.0° 23.50 eV 2.8833e+02 max 7.22 min
 C1s/Point2: SL2 50, Point 1/1

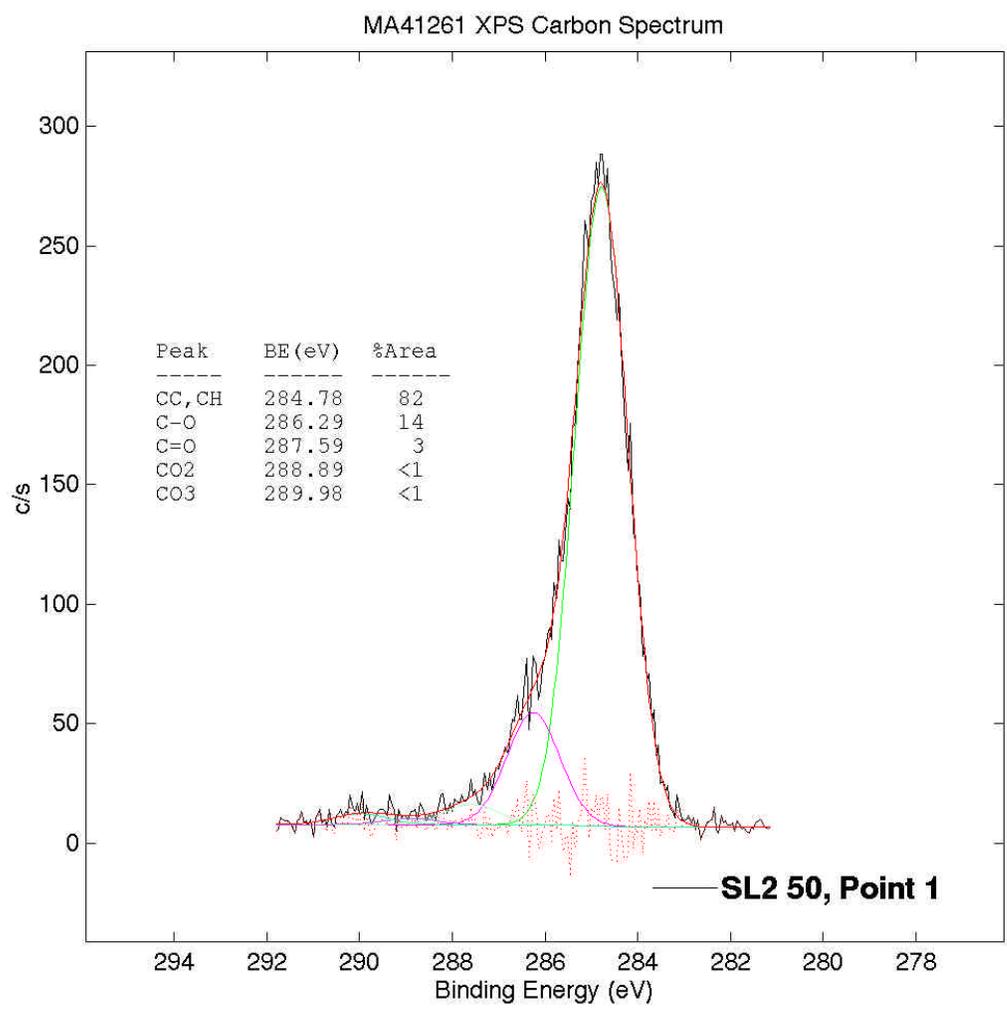


Figure 15. Precision XPS scan of the C1s peak on SL2_S0 wire sample. Considerable C-O bonds are present in the shoulder.

hrscan300.spe: Samples 03-30-2004.: etched ~5nm McCrone Assoc.
 2004 Mar 31 Al mono 1.3 W 5.0 μ 45.0° 23.50 eV 1.3267e+02 max 14.45 min
 C1s/Point9: SL2 50, Point 2/1

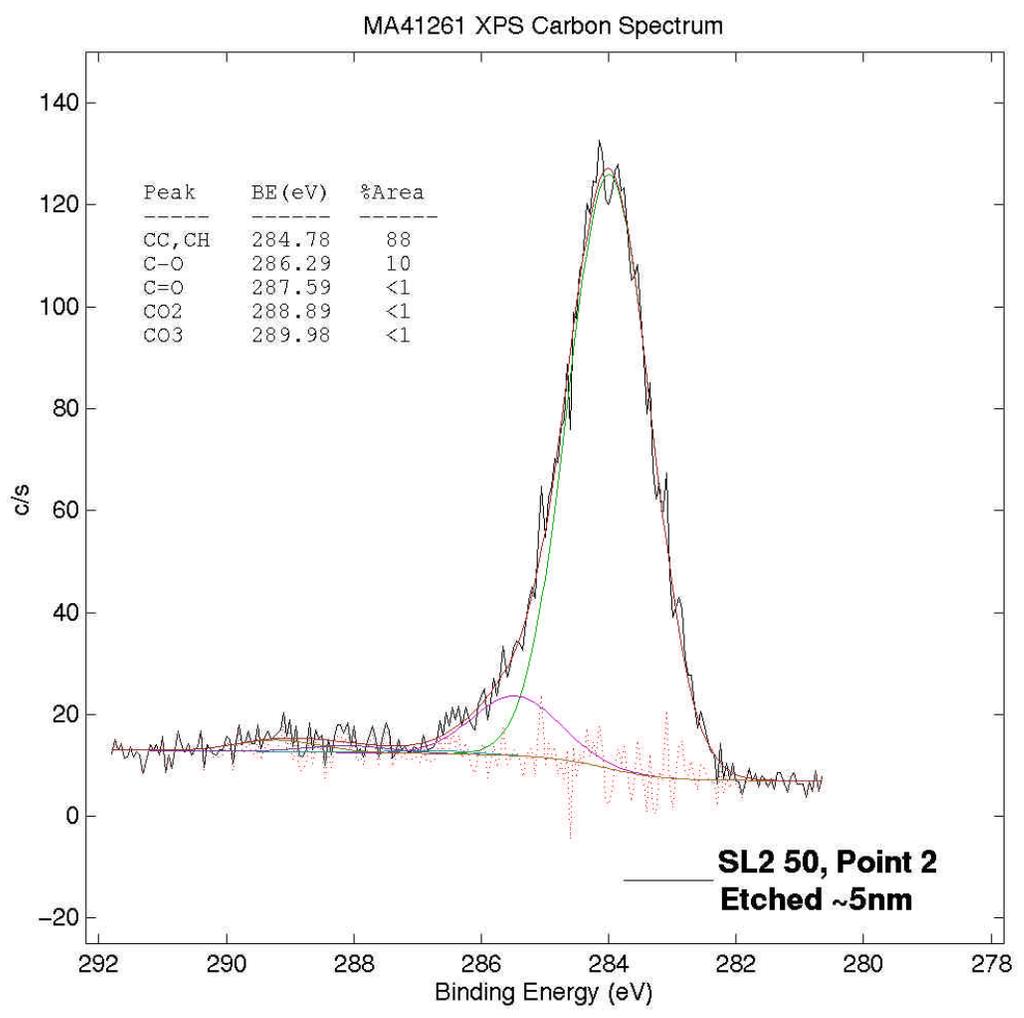


Figure 16. Precision XPS scan of the C1s peak on SL2_S0 wire sample after etching away about 5 nmeters of surface material using an argon ion beam. The C=O bonds are no longer apparent.

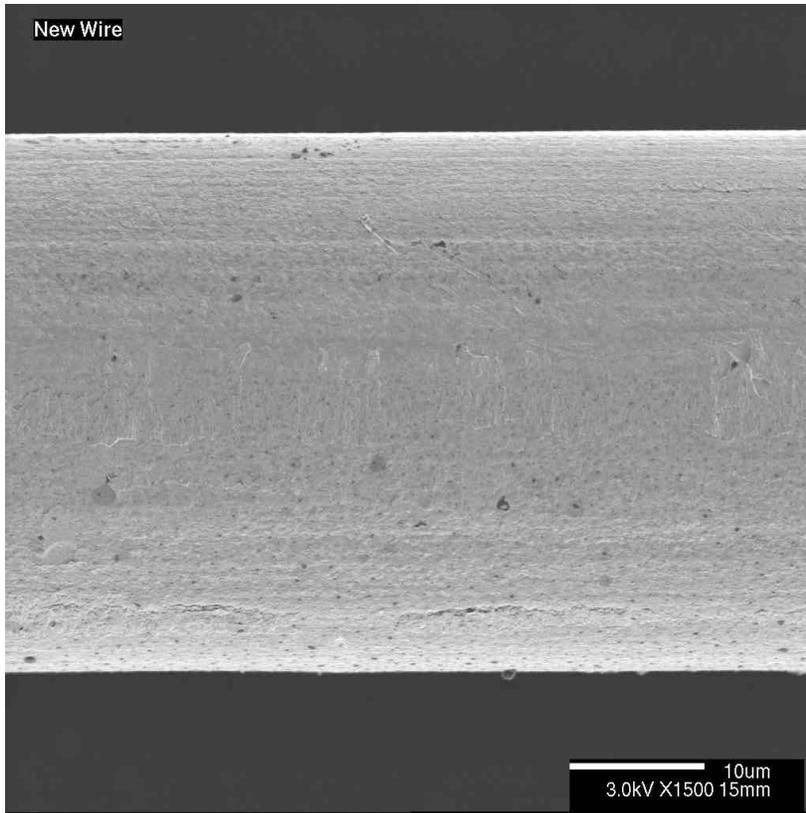


Figure 17. FSEM high resolution picture of a new wire using a precision electron beam.

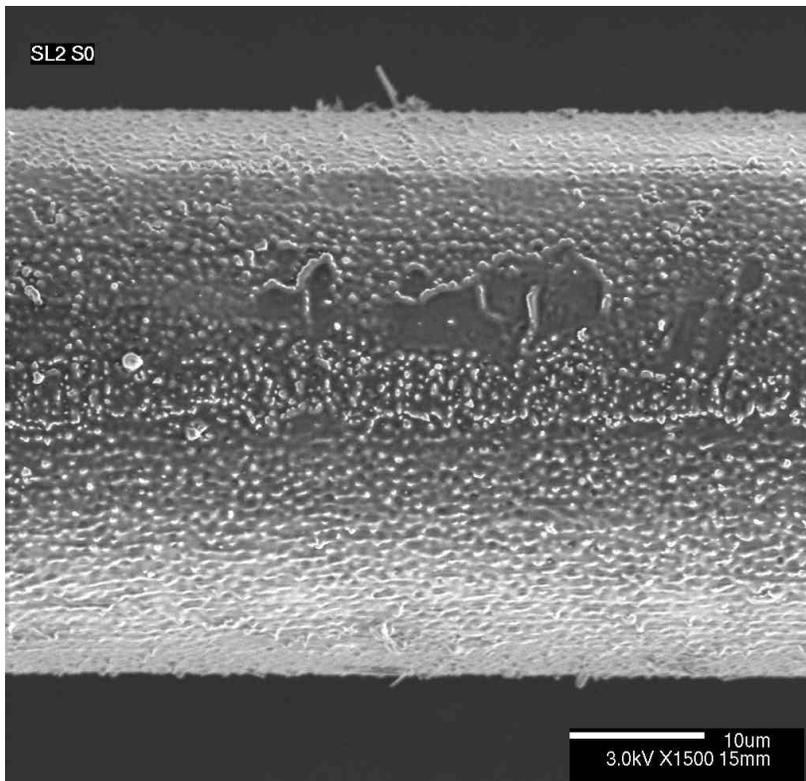


Figure 18. FESEM high resolution picture of SL2_S0. Lots of sub-micron nodules are seen.

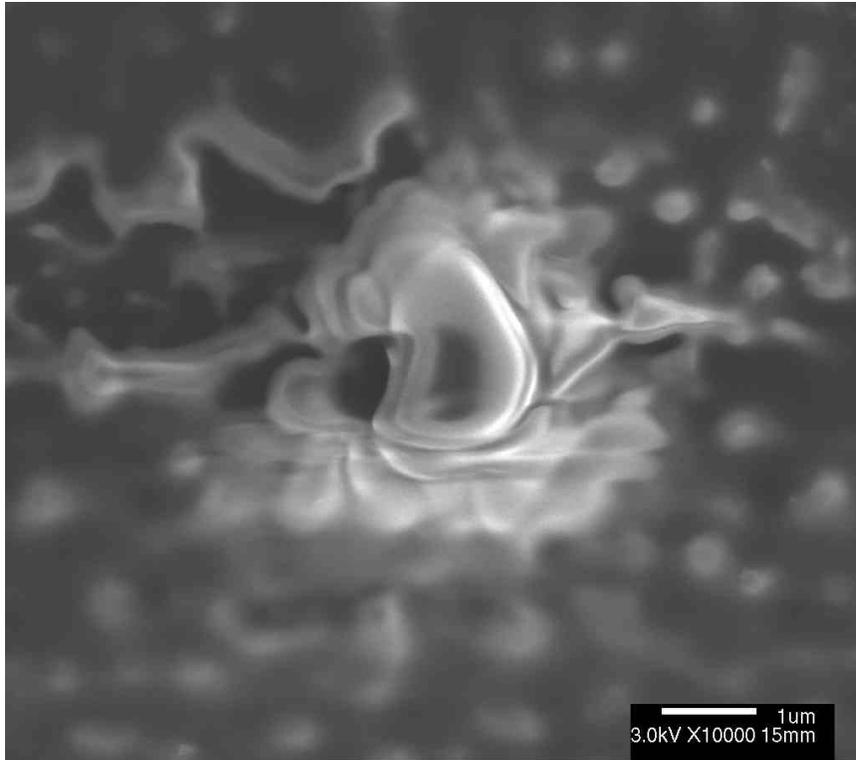


Figure 19. FESEM high resolution picture of SL2_S0 showing a large nodule.

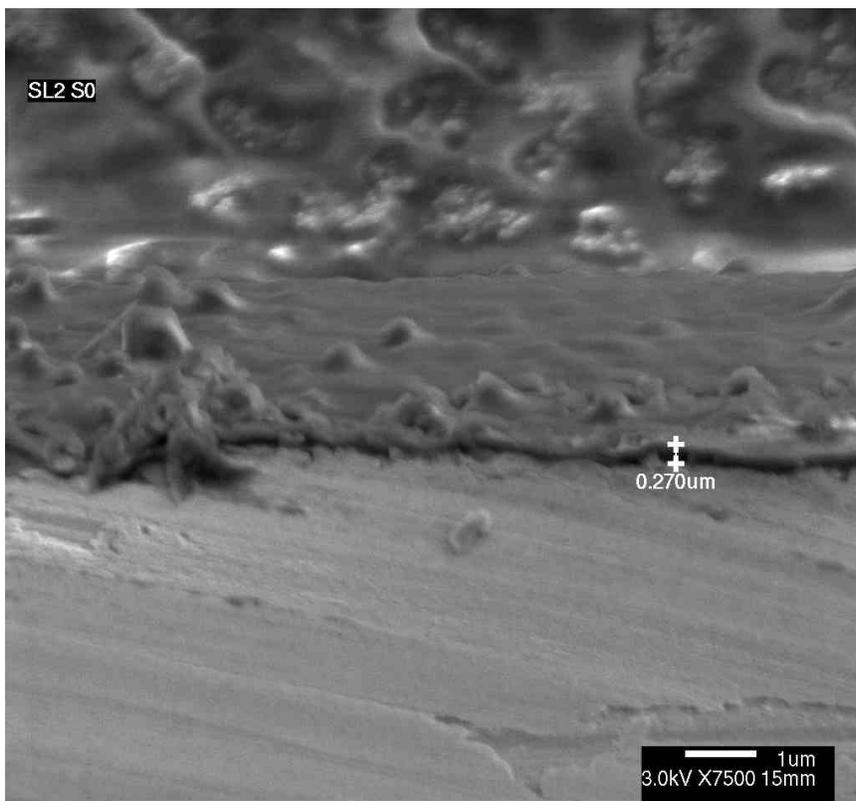


Figure 20 FESEM high resolution picture of SL2_S0. In the foreground the coating has been scraped off revealing bare wire. The dark coating with nodules is about 270 nm thick. In the background is tape.

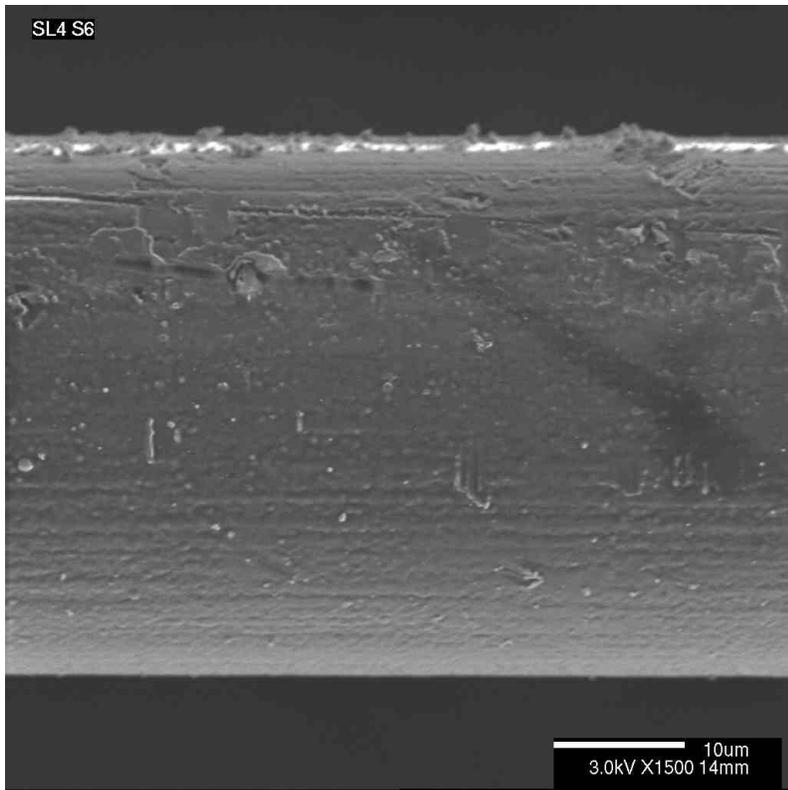


Figure 21 FESEM high resolution picture of SL4_S6. Thinner coating has fewer nodules.

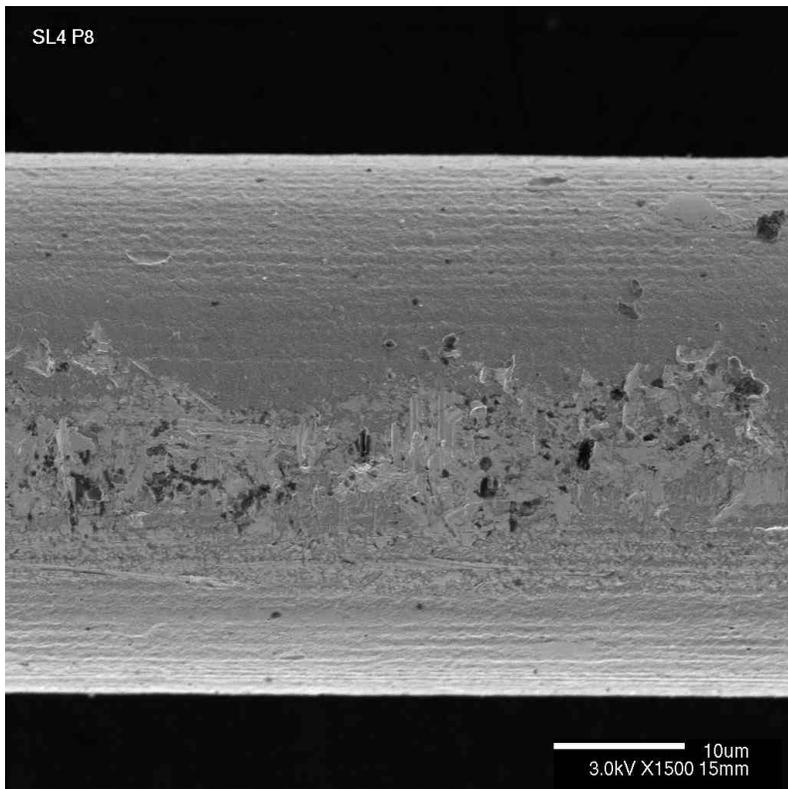


Figure 22. FESEM high resolution picture of SL4_P8. A dirty section of the wire is shown.

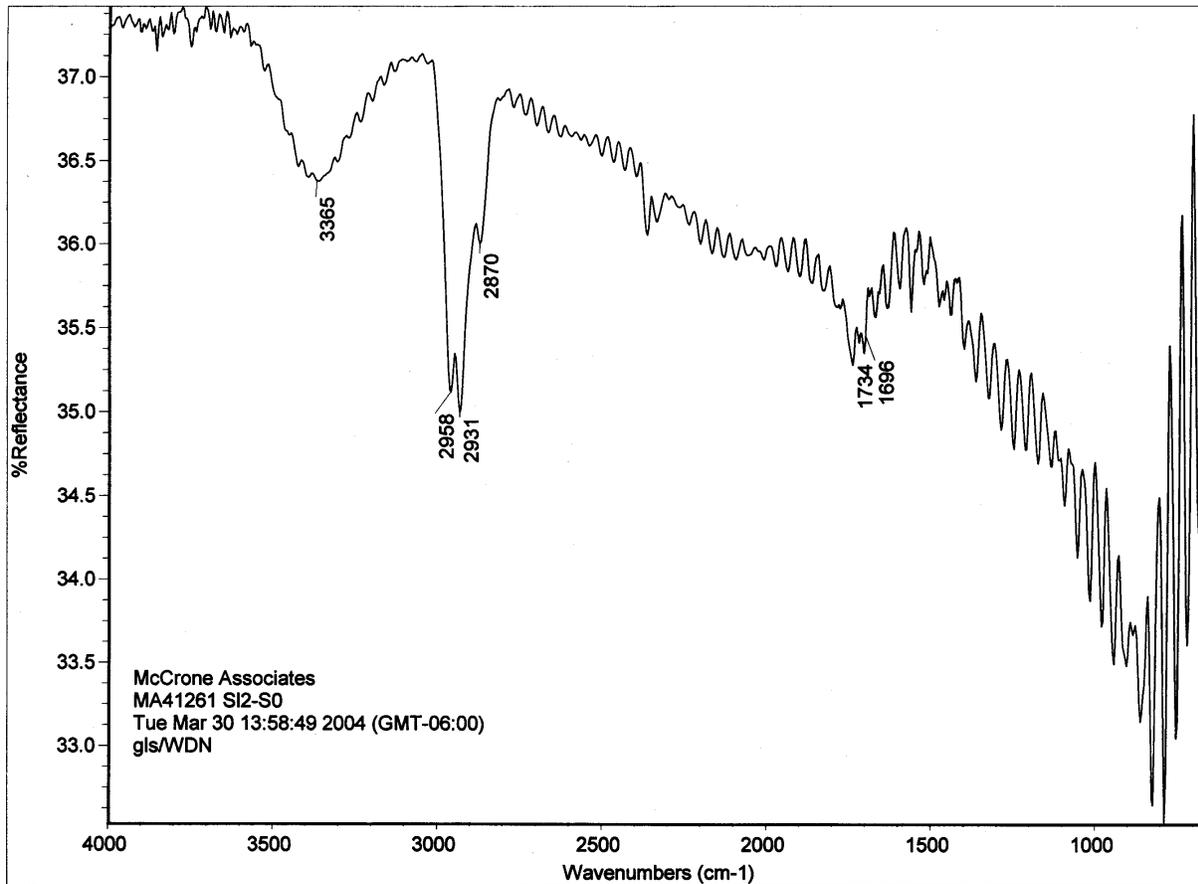


Figure 23. FTIR spectrum showing the absorption bands in reflected infrared light associated with molecular bonds. The broad dip at 3365 is the OH (stretching) bond. The dips at 2958, 2931, and 2870 are the CH₂ and CH₃ bonds. Two small dips at about 2300 are probably background CO₂. The dips at 1734 and 1696 are probably C=O bonds.